Development of 3TM NovecTM 612 Magnesium Protection Fluid as a Substitute for SF₆ over Molten Magnesium

Dean S. Milbrath

3M Performance Materials Division

For International Conference on SF6 and the Environment November 22, 2002

Protection of Molten Mg

- Molten salt fluxes protected melts, but contamination results in increased corrosion and low metal recovery
- Sulfur and SO₂ have been used for protection of molten Mg without added corrosion
- -1934, Reimers patented use of fluorine containing materials such as HF, BF₃, SiF₄, SbF₅, IF₅, PF₅, SO₂F₂, NF₃, or SF₆
- -1970-79 Fruehling started and Couling continued work to show SF₆ was effective
- -1998-2001 Cashion and SINTEF/Hydro workers described the surface films on Mg produced under SF₆ cover gases

SF₆ Protection of Molten Mg

$$Mg^{0} + O_{2} \longrightarrow MgO$$

$$Mg^{0} + SF_{6} \longrightarrow "MgF_{2}"$$

SF₆ Reactions over Mg?

 Compound CO2
 Lifetime (yrs)
 GWP (100 Yr ITH)

 100-150
 1

 25,200
 22,200

Compound		Lifetime (yrs)	GWP (100 Yr ITH)		
CO ₂		100-150	1		
SF ₆		3200	22,200		
C_3F_8		2600	8,600 7	PFCs	
C_4F_{10}		2600	8,600		
C ₆ F ₁₄		3200	9,000 🗆		

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CO_2	100-150	1		
SF ₆	3200	22,200		
C_3F_8	2600	8,600 PFCs		
C_4F_{10}	2600	8,600		
C_6F_{14}	3200	9,000 _		
CF ₃ CH ₂ F	13.6	1,600 HFCs		
CF ₃ CHF ₂	32.6	3,800		
CHF ₃	243	14,800 _		

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SF ₆	3200	22,200		
C_3F_8	2600	8,600	PFCs	
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CF ₃ CHF ₂	32.6	3,800	111 03	
CHF ₃	243	14,800 —		
$C_3F_7C(O)C_2F$	F ₅ 0.014	~1	FKs	

Fluorinated Ketone Physical and Environmental, Safety and Health Properties

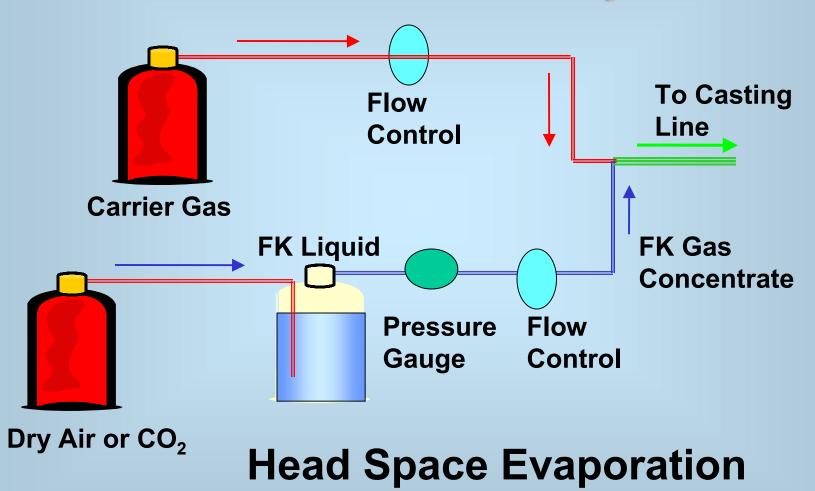
Physical Properties					
Boiling Point °C	49				
Freezing Point °C	-108				
Viscosity, liquid @ 20°C, cSt	0.042				
Vapor Pressure @ 20°C, kPa	32.6				
Liquid Density @ 20°C, g/mL	1.61				
Gas Density @ 80°C - 1 Atm, g/mL	0.011				

EHS Properties	5
Atmospheric lifetime, days	<10
Global Warming Poteintial	~1
Flash Point	None
PEL, ppmV	150
Acute LC50, ppmV	>100,000

Environmental

- NovecTM 612 : GWP = 1, Non-ozone depleting, short atmospheric lifetime (1 week)
- Degraded in sunlight to CO₂, HF and TFA
- Fully registered in Europe, US, Canada, Australia with no restrictions
- Registration in Japan early 2003

Liquid to Gas System to Generate Cover Gas System



NovecTM 612 Applications Experience

Tested over pure Mg, AM-50, RZ-5, AJ-52, AZ-91 With dry air, CO₂, N₂, Ar or mixtures as the carrier gas

At melt temperatures from 650 to 790 °C

In 3 to 500 kg furnaces with melt areas of 0.008 to 0.5 m²

For open casting (ingots and sand casting) and die casting

Pilot Scale Furnace



Surface of AM-50 in 80 kg Crucible

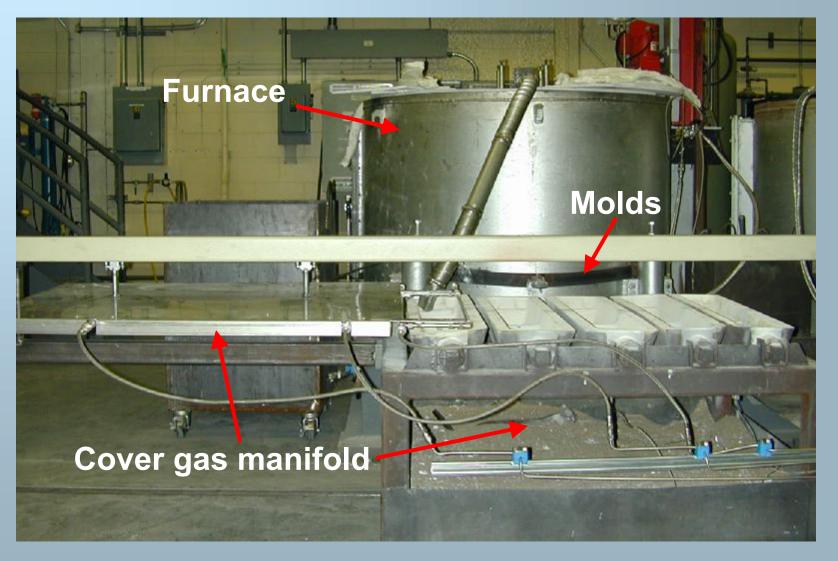


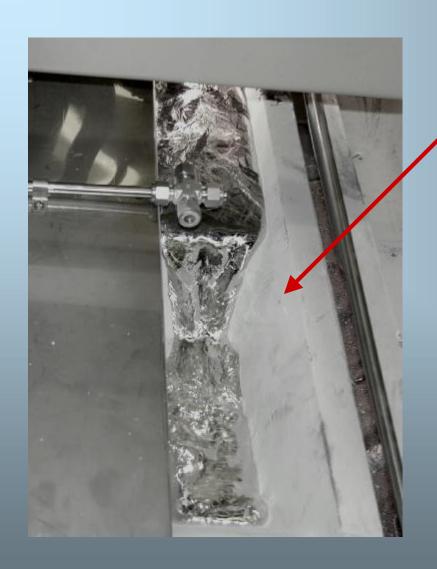
Hand casting of AM-50



Under 500 ppmV of FK in CO₂ @ 30 CFH

Ingot Casting Setup





Under 750 ppmV FK in CO₂ @ 90 CFH

Ingot mold filling with pumped molten Mg



Protection Summary

Mg protection similar to that produced by SF₆ (Operators' Comments)

Protected at lower conc and flow rates

SF₆ (0.2 to 2.0%)

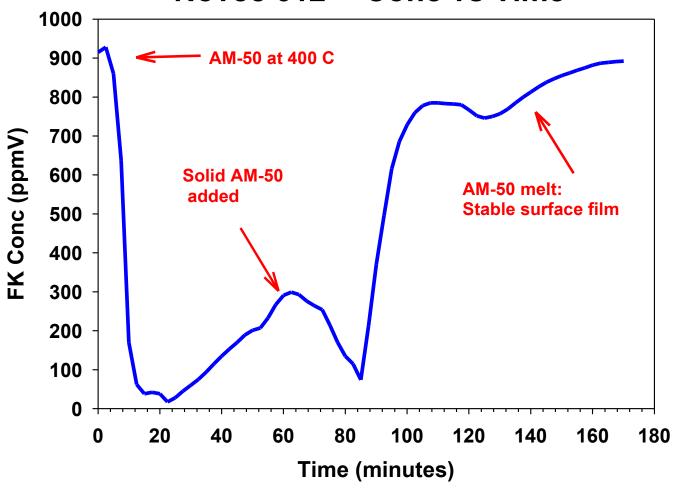
NovecTM 612 (0.025 to 0.1%)

Spot oxidation/fires extinguished with higher flow rates of NovecTM 612

Protected all casting operations tested

Reactions of NovecTM 612 "MgF₂" + CO₂ -CO >575 C $C_2F_5-C-C_3F_7$ CO₂ + HF + TFA PFCs F-Olefins

Initial Melt of AM-50 Ingots Novec 612TM Conc vs Time



Emissions from Casting Trials

	Conditions			Gas Analysis			
Alloy	FK	Flow	Ingot	FK	PFIB	PFC	HF
	Conc	Rate	Quality	found	Found	Found	Found
	(ppmV)	(CFH)		ppmV	ppbV	ppmV	ppmV
AM-50	500	30	Good	4	Not Det	-	10
AM-50	250	30	Marginal	1	Not Det	-	-
Pure Mg	750	90	Good	4	Not Det	Not Det	-
Pure Mg	1000	90	Good	14	Not Det	Not Det	-
Pure Mg	500	20	Poor	9	Not Det	Not Det	-

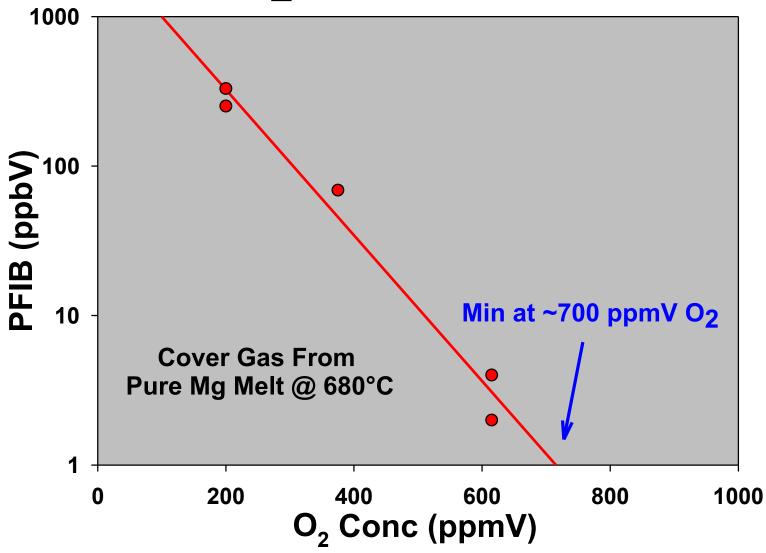
CO₂ as carrier gas

Composition In Furnace

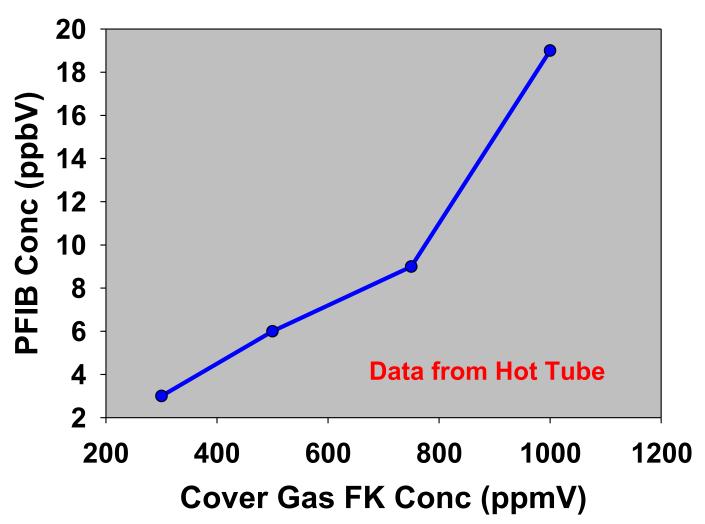
	Conditions			Gas Analysis			
Alloy	Melt	FK	Flow	Furnace	FK	PFIB	PFC
	Temp	Conc	Rate	Protection	found	Found	Found
	(°C)	(ppmV)	(CFH)		ppmV	ppbV	ppmV
AM-50	680	1000	20	Good	894	204	-
AJ-52	720	1000	10	Good	164	26	322
Pure Mg	680	1000	20	Good	23	23	380
Pure Mg							
skimmed	680	1000	20	Good	1	Not Det	Not Det

CO₂ as carrier gas

Effect of O₂ Content of Cover Gas



Effect of FK Conc on PFIB Formation



Control of F-Olefin Production

- Oxygen in the cover gas mixture (1-5% air) for furnaces
- Use low concentration of FK (higher flow rates)
- Increase flow rate not concentration
- Don't overprotect

Furnace Gas Composition over AM-50

AM-50 @ 6	80°C with 5				
Gas	Novec 612	PFC	F-Olefin	COF2	HF
Flow rate	Conc	Conc	Conc	Conc	Conc
2.5	22 ± 5	25 ± 7	ND	ND	84 ± 19
L/min	ppmV	ppmV			ppmV

From SINTEF Pilot Trials 9/2002

- Melt is over protected at these conditions
- HF generation is under study

Beta-site tests are underway

Testing at user sites to produce useful information on use conditions and performance.

Sites chosen to broaden application types and uses to confirm efficacy and refine designs of application equipment.

Continued Cooperation with IMA Program

Commercial Introduction 3TM NovecTM 612 Magnesium Protection Fluid

Phased Market Introduction 2003
North America, Europe, Japan
Full production in 1st Quarter 2003
Pilot supplies are available now
Technical Support for Conversions

Acknowledgement

The author wants to thank the generous support by Noranda Technical Center and specifically Eric Richard and Don Argo and by the Norsk Hydro Light Metals Research Centre and Sten Bjorneboe and Haavard Gjestland for the molten magnesium experiments and well as Gabriella Tranell and Bjarte Oye of SINTEF for teaching a bit of metallurgy to a chemist.